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**FILE**  
OFFICE OF  
PREVENTION, PESTICIDES AND  
TOXIC SUBSTANCES

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**MEMORANDUM:**

**SUBJECT:** Review of data on dissipation of dislodgeable residues of  
Pyridaben [BASF 300 11] from citrus foliage in Texas,  
California, and Florida

**TO:** Michael Metzger, Chief  
Risk Assessment and Characterization Branch  
Health Effects Division (7509C)

**FROM:** James D. Adams, Ph.D., Chemist

*James D. Adams*

**THRU:** Mark Dow, Ph.D., Section Chief  
Special Review Registration Section II

*Mark Dow*

Edward Zager, Chief  
Occupational and Residential Exposure Branch  
Health Effects Division (7509C)

*Jusen U. Hummel, acting for*

Please find below, the OREB review of:

DP Barcode: D220277

Pesticide Chemical Code: 129105

EPA Reg. No.: 7969-106

EPA MRID No.: 436804-25

PHED: N/A

## **I. INTRODUCTION:**

### **A. Background:**

Pyridaben [(butyl)-5-(4-tert-butyl-benzylthio)-4-chloropyridazin-3-(2H)one] is a miticide/insecticide registered for use on a number of crops including citrus. On October 18, 1995, EPA issued a generic Data-Call-In for data on Pyridaben with respect to field-worker protection. These requirements include foliar residue dissipation (§ 132-1(a); dermal dosimetry (§ 133-3); and inhalation dosimetry (§ 133-4).

### **B. Purpose:**

The Registrant [BASF] has submitted data for several crops to cover requirements discussed in Guideline Subdivision K - "Exposure: Reentry Protection" and required under Title 40 of the Code of Federal Regulations; Section 158.390. However, the submission reviewed here (DP Barcode D220277; MRID 436804-25) contains data for the dissipation of foliar dislodgeable residues (FDRs) from citrus foliage. Human exposure data were not gathered in conjunction with these dissipation studies.

## **II. DETAILED CONSIDERATIONS:**

### **PESTICIDE APPLICATIONS AND SITES**

FDR dissipation studies were conducted on navel orange trees in California's Fresno County, on hamlin orange trees in Florida's Seminole County, and on grapefruit trees in Texas's Willacy County. Those studies have been reviewed and reported on by Versar, and that report is relied on in this review. All of the following page references are to those page numbers assigned in MRID 436804-25.

The choice of the sites is acceptable since they are in environments representative of the areas growing citrus in those states. The study in Fresno County is the only study necessary since it is in the San Joaquin Valley. That valley is one of the inland environments of California that has had the lowest pesticide dissipation rates in the nation and among the highest field-worker exposure rates as a result. The Registrant's choice to conduct dissipation studies in other environments is allowed under Subdivision K and affords opportunity to establish appropriate but, perhaps, shorter Restricted Entry Intervals (REIs) in higher rainfall and higher humidity environments.

The pesticide was applied at all three sites by airblast application as BAS 300 11 I at the rate of 0.495 lbs of active ingredient per acre in 160 gallons of finish spray [pp. 39, 42]. BAS 300 11

I is an end use product containing 75% ai of pyridaben by weight intended for the treatment of citrus. Each site was treated twice at the maximum rate allowed on the label 0.495 lbs ai/acre] with the applications 30 days apart. This was done to provide samples that could result from residue accumulation between the two applications allowed on labels. Although the label requires a 90-day interval between 0.495 lbs ai/acre applications for field practice, the 30-day interval used in these studies is acceptable since the FDR levels could only be higher at the onset of the dissipation studies. This would tend to lead to longer REIs.

#### FIELD SAMPLING AND ANALYTICAL PROCEDURES

A major concern with this submission is the high variability and low recoveries reported for the residues. For example, recoveries reported for the Texas field spikes range from 10.1% to 120% [pp. 210, 211] with an average of 62.18 and a standard deviation of 19.44 for 36 samples. The Florida recoveries [pp. 209, 210] are better with an average of 63.55 and a standard deviation of 18.34 for 36 samples, but the California recoveries [pp. 206, 208] are best with an average of 67.87 and a standard deviation of 11.68 for 36 samples [cf. TABLE I below]. Ideally average recoveries should approach 100% and have a low standard deviation.

TABLE I

STATISTICAL ANALYSIS OF FIELD SAMPLE RECOVERIES				
STATISTICS	CALIFORNIA	FLORIDA	TEXAS	ALL SITES
AVERAGES	67.87	63.55	62.18	64.53
STD DEV	11.68	18.34	19.44	17.01
NUMBER	36	36	36	109

Part of these low average recoveries may be the result of inherent properties of pyridaben. BASF Corp reports [p. 370] that pyridaben adsorbs to glass and that it is light sensitive so residue samples for analysis must be protected from light by storage in amber glass [cf. page 188]. However, there are other possible reasons for the low average recoveries.

The "dislodgeable residue procedure" used in these studies.

The three articles [Gunther, et al. (1973); Gunther, et al. (1974); and Iwata, et al. (1977)] listed below are the basis of the "Dislodgeable Residue" procedure required in Subdivision K for the quantification of foliar residues and their dissipation. This procedure is also critical for the prediction of fieldworker exposure rates. In all three of those papers, leaf-punch samples were

water-washed three times.

In the submitted pyridaben studies, leaf punches were only water-washed twice [submission page 8]. There are other variations in the procedure including use of an aqueous solution of "Aerosol OT 75®" [AOT] solution. There does not appear to have been any care taken to ensure the transfer of particulates from the leaf washes, in fact the samples were filtered at one point in the procedure. Iwata, et al. (1977) make a special point about the need for transfer of the particulates up to the extraction step and to the fact that FDRs are frequently sorbed to particulates.

### **The analytical procedure used in these studies**

The Registrant has submitted [p. 195] fortification data that indicate that their analytical procedure can yield acceptable data. The recoveries there range from 93.8 to 104% with an average of 98.8 and a standard deviation of 3.74 for 12 samples.

One possible reason for the low recoveries reported is a problem with the analytical procedure in the evaporation of a residue sample to dryness. Evaporation of the residues to dryness by blow drying [pp. 370, 376] after the partition of residue samples may result in low analytical results for two reasons. It has been found with other pesticide residue analyses that passing warm/hot air over a concentrated sample tends to enhance volatilization; and heat from the drying can increase the rate of pesticide degradation. It is common practice in some laboratories doing pesticide residue analyses to add a few drops of a low-volatility oil as a "keeper" to minimize sample loss during evaporation.

### **LEVELS OF FIELD SAMPLE FDRS**

It is possible to correct for the low recoveries discussed above by dividing the reported FDRs by the appropriate recoveries as a decimal fraction. However, the recoveries used in the submission are not appropriate for these corrections.

Recoveries should be done in company with the appropriate field residue samples in order to adjust the FDR levels with the recoveries. This is done under the assumption that the recovery and FDR samples were treated the same way and would have the same percentages of loss. However, field samples were fortified with standard solutions [for recovery data] on the day before the final application and on days 0, 7, 17, 34/35, and 70 (6 samples each date) after pesticide application [pp. 206-211]. These recovery data were then averaged in the submission to yield an average of 72.6% recovery which was used to correct field FDR levels. This is not acceptable.

In the submission, the "corrected" average FDRs were converted to natural logarithms (LNs) for linear regression with the DAAs. Use of this type of correlation has become a standard procedure for expression of the dissipation of residues, but as the Registrant states it frequently does not yield a linear relationship since the dissipation is not a homogenous reaction. In all three of the states, the dissipation graphs curve. Nevertheless, the graphs are useful for examination of the data to visually compare dissipations of the FDRs in the three different environments.

The Registrant also analyzed the "corrected" FDR data by regression analysis. This yielded two equations which together describe the residue dissipation. This is an innovative approach and is defensible from both mathematics and chemical kinetics. That analysis, unfortunately, is not useful here since it is based on unacceptable FDR data.

In the following tables, the three replicate FDR values reported for each site and Day After Application (DAA) have been averaged and then divided by the appropriate (for site and DAA) recovery as a decimal fraction. In most cases, this constituted an increase of reported FDR levels by about one third. Appropriate recoveries for these data are taken to be the recovery for the sample date or the average of the two recoveries before and after the sample date. FDR levels were converted to human exposures assuming an 8-hour day and a transfer factor of 10,000.

TABLE II

Exposure to Pyridaben Residues on California Citrus Foliage						
DAA	FDR #1	FDR #2	FDR #3	FDR avg $\mu\text{g}/\text{cm}^2$	Percent Recovery	EXPOSURE mg/day
0	1.1	1.48	1.12	1.233	71.83	137.4
1	1.24	1.16	1.11	1.170	70.6	132.6
2	1.15	0.731	0.949	0.943	70.6	106.9
3	0.801	0.846	0.599	0.749	70.6	84.83
4	0.642	0.689	0.583	0.638	70.6	72.29
5	0.598	0.486	0.486	0.523	70.6	59.30
7	0.547	0.533	0.718	0.599	69.37	69.12
9	0.413	0.301	0.298	0.337	70	38.55
11	0.313	0.334	0.351	0.333	70	38.02
13	0.384	0.287	0.298	0.323	70	36.91
15	0.249	0.33	0.244	0.274	70	31.35
17	0.226	0.259	0.254	0.246	70.62	27.91
20	0.403	0.322	0.317	0.347	61.88	44.9
24	0.419	0.112	0.145	0.225	61.88	29.13
28	0.125	0.153	0.218	0.165	61.88	21.37
34	0.101	0.059	0.145	0.102	53.13	15.31
40	0.115	0.032	0.067	0.071	61.77	9.24
50	0.0482	0.03	0.0523	0.044	61.77	5.63
70	0.0316	0.0551	0.03	0.039	70.4	4.42

TABLE III

Exposure to Pyridaben Residues on Florida Citrus Foliage						
DAA	FDR #1	FDR #2	FDR #3	FDR avg, $\mu\text{g}/\text{cm}^2$	Percent Recovery	EXPOSURE mg/day
0	0.818	0.989	0.716	0.841	71.83	93.67
1	0.131	0.113	0.126	0.1233	70.60	13.98
2	0.115	0.13	0.0967	0.1139	70.60	12.91
3	0.0976	0.0683	0.0569	0.07426	70.60	8.42
4	0.099	0.11	0.0962	0.10173	70.60	11.53
5	0.099	0.0764	0.0621	0.07916	70.60	8.97
7	0.042	0.0309	0.0225	0.0318	69.37	3.67
9	0.0341	0.00614	0.0224	0.02088	70.00	2.39
11	0.0275	0.03	0.0269	0.028133	70.00	3.22
13	0.00694	0.0459	0.0216	0.024813	70.00	2.84
15	0.0143	0.0150	0.0156	0.014967	70.00	1.71
17	0.00454	0.00899	0.00168	0.00507	70.62	0.57
20	0.00437	0.00691	0.01250	0.007927	61.88	1.02
24	0.01150	0.000002	0.00596	0.005820	61.88	0.75
28	0.00114	0.00549	0.01120	0.005943	61.88	0.77
35	0.00506	0.000020	0.00375	0.002943	53.13	0.44
40	0.00002	0.00325	0.00002	0.001097	61.77	0.14
50	0.00003	0.00002	0.00185	0.000633	61.77	0.08
70	0.000005	0.000005	0.000005	0.000005	70.40	0.00057

TABLE IV

Exposure to Pyridaben Residues on Texas Citrus Foliage						
DAA	FDR #1	FDR #2	FDR #3	FDR Avg $\mu\text{g}/\text{cm}^2$	Percent Recovery	EXPOSURE, Mg/Day
0	0.737	1.0	0.682	0.806	72.6	88.85
1	0.539	0.534	0.61	0.561	72.6	61.82
2	0.107	0.108	0.196	0.137	72.6	15.10
3	0.157	0.0419	0.0356	0.078	68.67	9.11
4	0.0883	0.0846	0.0851	0.086	72.6	9.48
5	0.0586	0.0445	0.0517	0.052	70.63	5.84
7	0.093	0.0614	0.0717	0.075	72.6	8.30
9	0.0563	0.0657	0.0482	0.057	70.63	6.42
11	0.0548	0.0879	0.0368	0.060	70.63	6.78
13	0.0847	0.0469	0.0317	0.054	68.67	6.34
15	0.0426	0.0281	0.0692	0.047	70.63	5.28
17	0.032	0.0453	0.042	0.040	66.7	4.77
20	0.0176	0.0220	0.0336	0.024	58.43	3.34
24	0.021	0.0345	0.0208	0.025	58.43	3.48
28	0.0252	0.0279	0.0121	0.022	62.56	2.78
34	0.0183	0.0317	0.0268	0.026	62.56	3.27
40	0.0222	0.0191	0.0251	0.022	58.43	3.03
50	0.00667	0.00989	0.00879	0.008	54.3	1.24
70	0.00558	0.00558	0.0139	0.008	54.3	1.23

### III. CONCLUSIONS/RECOMMENDATIONS:

The submitted data are acceptable only when corrected for the low recoveries reported. Daily exposure data reported in Tables I, II, and III can be used to calculate margins of safety for each date and site using the appropriate toxicology data. This is being done in connection with review of MRID 436804-26 for establishment of REIs.

A comparison of the daily exposures estimated from the submitted data shows that pyridaben dissipation is fastest in Florida, intermediate in Texas, and slowest in California. This trend tends to agree with FDR dissipation data for other pesticides. Therefore, REIs for pyridaben may be shorter for Florida and Texas than for California.

#### IV. REFERENCES:

Gunther, F.A., W.E. Westlake, J.H. Barkley, W. Winterlin, and L. Langbehn. 1973. Establishing dislodgeable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 9:243-249.

Gunther, F.A., J.H. Barkley, and W.E. Westlake. 1974. Worker environment research. II. Sampling and processing techniques for determining dislodgable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 12(6): 641-644.

Iwata, Y., J.B. Knaak, R.C. Spear, and R.J. Foster. 1977. Worker Reentry into Pesticide Treated Crops. I. Procedure for the Determination of Dislodgable Pesticide Residues on Foliage. Bull. Environ. Contam. Toxicol. 18, 649-655.

CC: Jack Housenger, SRRD 7508W  
Correspondence File  
**Pyridaben** File [129105]  
James D. Adams, OREB